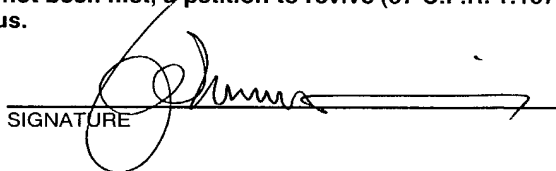


JCO7 Rec'd PCT/PTO 11 MAR 2002

FORM PTO-1390 (REV 11-2000)	U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 687-104
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5) 10/070826 Unassigned
INTERNATIONAL APPLICATION NO. PCT/GB00/03449	INTERNATIONAL FILING DATE 8 September 2000	PRIORITY DATE CLAIMED 10 September 1999 and March 22, 2000
TITLE OF INVENTION COMPOSITE ION-EXCHANGE MEMBRANES		
APPLICANT(S) FOR DO/EO/US WILSON et al		
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. <input type="checkbox"/> The U.S. has been elected by the expiration of 19 months from the priority date (Article 31). A copy of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). <input type="checkbox"/> has been communicated by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> <input type="checkbox"/> is attached hereto. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)). <ol style="list-style-type: none"> <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). <input type="checkbox"/> have been communicated by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> A English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). <p>Items 11 To 20 below concern document(s) or information included:</p> <ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). <input type="checkbox"/> Other items or information. 		

JG13 Rec'd PCT/PTO 11 MAR 2002

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.53) Unassigned 10070826		INTERNATIONAL APPLICATION NO PCT/GB00/03449		ATTORNEY'S DOCKET NUMBER 687-104	
21. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 C.F.R. 1.492(a)(1)-(5): -- Neither international preliminary examination fee (37 C.F.R. 1.482) nor international search fee (37 C.F.R. 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.....\$1040.00 -- International preliminary examination fee (37 C.F.R. 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....\$890.00 -- International preliminary examination fee (37 C.F.R. 1.482) not paid to USPTO but international search fee (37 C.F.R. 1.445(a)(2)) paid to USPTO.....\$740.00 -- International preliminary examination fee (37 C.F.R. 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4).....\$710.00 -- International preliminary examination fee (37 C.F.R. 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4).....\$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				\$	1040.00
				\$	130.00
				Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 C.F.R. 1.492(e)).	
				\$	130.00
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	25	-20 =	5	X	\$18.00
Independent Claims	2	-3 =	0	X	\$84.00
MULTIPLE DEPENDENT CLAIMS(S) (if applicable)					\$280.00
TOTAL OF ABOVE CALCULATIONS =				\$	1260.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.					0.00
SUBTOTAL =				\$	1260.00
Processing fee of \$130.00, for furnishing the English Translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 C.F.R. 1.492(f)).				+	0.00
TOTAL NATIONAL FEE =				\$	1260.00
Fee for recording the enclosed assignment (37 C.F.R. 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. 3.28, 3.31). \$40.00 per property				+	0.00
Fee for Petition to Revive Unintentionally Abandoned Application (\$1280.00 - Small Entity = \$640.00)				\$	0.00
TOTAL FEES ENCLOSED =				\$	1260.00
				Amount to be:	
				refunded	\$
				Charged	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$1260.00 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. 14-1140 in the amount of \$_____ to cover the above fees. A duplicate copy of this form is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 14-1140. A duplicate copy of this form is enclosed. d. <input checked="" type="checkbox"/> The entire content of the foreign application(s), referred to in this application is/are hereby incorporated by reference in this application.					
NOTE: Where an appropriate time limit under 37 C.F.R. 1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: NIXON & VANDERHYTE P.C. 1100 North Glebe Road, 8 th Floor Arlington, Virginia 22201-4714 Telephone: (703) 816-4000 LCM:lks					
<div style="border: 2px solid black; padding: 5px; transform: rotate(-2deg); display: inline-block;"> The PTO did not receive the following listed item(s) \$ 11170 - Check </div>				 SIGNATURE	
				Leonard C. Mitchard NAME	
				29,009 March 11, 2002 REGISTRATION NUMBER Date	

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

WILSON et al

Atty. Ref.: 687-104

Serial No. Unassigned

Group:

Filed: March 10, 2002

Examiner:

For: COMPOSITE ION-EXCHANGE MEMBRANES

* * * * *

March 11, 2002

Assistant Commissioner for Patents
Washington, DC 20231

Sir:

PRELIMINARY AMENDMENT

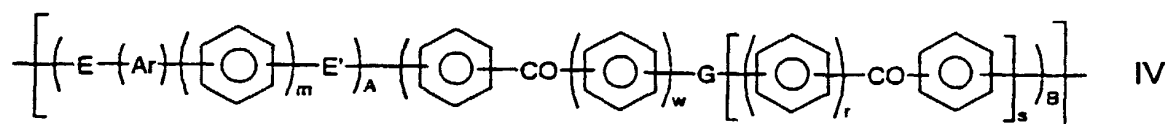
Please amend the above application as follows:

IN THE CLAIMS

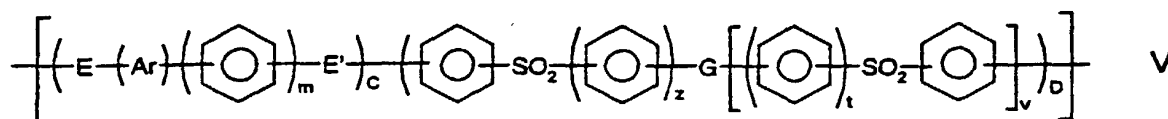
Please substitute the following amended claims for corresponding claims previously presented. A copy of the amended claims showing current revisions is attached.

3. (Amended) A membrane according to claim 1 , wherein said first conductive polymer is crystalline.

4. (Amended) A membrane according to claim 1, wherein said polymer is a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV and/or V

wherein A, B, C and D independently represent 0 or 1.

5. (Amended) A membrane according to claim 1, wherein said first conductive polymer includes at least some ketone moieties in the polymeric chain.

6. (Amended) A membrane according to claim 1, wherein said first conductive polymer is a copolymer comprising a first repeat unit which is selected from the following:

(a) a unit of formula IV wherein E and E' represent oxygen atoms, G

represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

(c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and O represent 1;

(d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

(e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

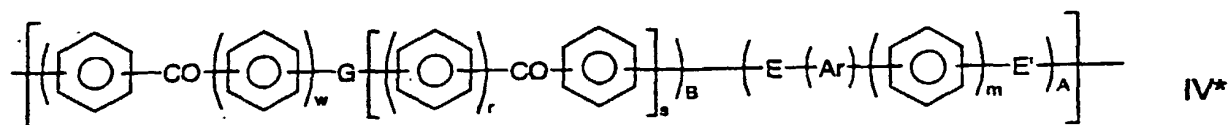
(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

(h) a unit of formula V wherein E and E' represent oxygen atoms, G

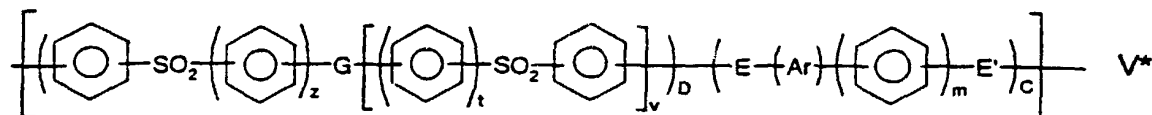
represents a direct link, Ar represents a moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

8. (Amended) A membrane according to claim 1, wherein said first conductive polymer is a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV* and/or V* wherein A, B, C and D independently represent 0 or 1.

9. (Amended) A membrane according to claim 1, wherein said first conductive polymer includes a biphenylene moiety.

10. (Amended) A membrane according to claim 1, wherein said first conductive polymer includes a -O--biphenylene-O-moiety.

11. (Amended) A membrane according to claim 1, wherein a film of said conductive polymer is laminated to the support material.

12. (Amended) A membrane according to claim 1, wherein the support material is porous and said conductive polymer is impregnated in the support material.

13. (Amended) A membrane according to claim 1, wherein said support material comprises a polymer having a moiety of formula I, II and/or III as described in claim 1 except that the polymer of the support material is either not sulphonated (or otherwise functionalised to provide ion-exchange sites) or is only sulphonated (or otherwise functionalised to provide ion—exchange sites) at or in the region of the surface of the support material.

14. (Amended) A membrane according to claim 1, wherein said support material is selected from the following homopolymers of formula IV as shown in claim 4:

- E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1

- E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero

- Ar represents a moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1.

- Ar represents a structure (i)*, E represents an oxygen atom, E' represents a direct link, m represents 0, A represents 1, B represents 0.

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- Ar represents moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents zero, w represents 1, r represents 0, s represents 1 and A and B represent 1

- Ar represent moiety (iv); E represents a sulphur atom, m represents 0, E' represents a direct link and B represents 0;

or is selected from:

- a homopolymer of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; and is selected from:

- polysulphone for example comprising a homopolymer of formula V wherein E and E' represent oxygen atoms, m represents zero, C and D represent 1, z represents 1, G represents a direct link, v represents zero and Ar represents a moiety of structure:

15. (Amended) A membrane according to claim 1, wherein said first conductive polymer has an equivalent weight (EW) of less than 800g/mol, preferably less than 500 g/mol.

17. (Amended) A fuel cell or electrolyser incorporating a composite membrane according to claim 1.

18. (Amended) A method of making a composite membrane according to

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claim 1, the method comprising causing a conductive polymer as described above to be associated with a support material as described above.

20. (Amended) A method according to claim 18 , wherein a first solvent formulation comprises a polar aprotic solvent in which a conductive polymer is provided and said support material is a material (e.g. a polyetheretherketone fabric or a polyetherketone microporous membrane) which is not soluble in said polar aprotic solvent, wherein the method includes a step of contacting said support material with said first solvent formulation.

21. (Amended) A method according to claim 18 , wherein said support material is a fabric and the method includes a step of contacting the fabric with a first solvent formulation comprising a first solvent and said conductive polymer, wherein said first solvent and said support material are selected so that the first solvent solubilizes a surface of the support material.

24. (Amended) A method according to claim 18 , the method including:
contacting said support material with a solvent formulation comprising a first solvent which solubilizes the support material; and
contacting the support material with a second solvent to cause phase inversion and render said support material porous.

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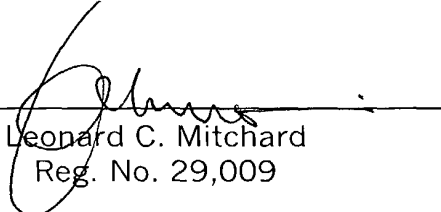
REMARKS

The above amendments have been made to place the application in a more traditional format. Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached pages are captioned **"Version With Markings To Show Changes Made."**

Respectfully submitted,

NIXON & VANDERHYE P.C.

By: _____


Leonard C. Mitchard
Reg. No. 29,009

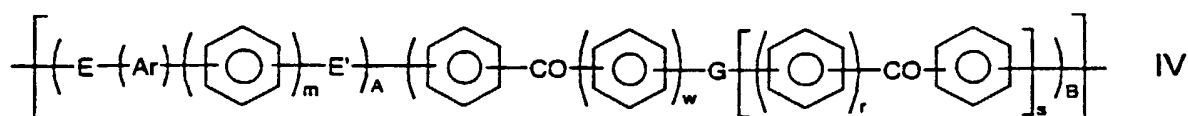
LCM:lks
1100 North Glebe Road, 8th Floor
Arlington, VA 22201-4714
Telephone: (703) 816-4000
Facsimile: (703) 816-4100

VERSION WITH MARKINGS TO SHOW CHANGES MADE

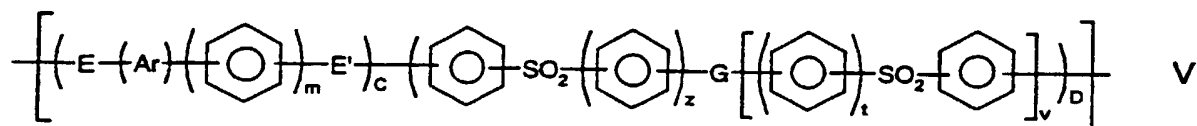
IN THE CLAIMS

3. (Amended) A membrane according to claim 1 [or claim 2], wherein said first conductive polymer is crystalline.

4. (Amended) A membrane according to [any preceding claim] claim 1, wherein said polymer is a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV and/or V

wherein A, B, C and D independently represent 0 or 1.

5. (Amended) A membrane according to [any preceding claim] claim 1, wherein said first conductive polymer includes at least some ketone moieties in

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the polymeric chain.

6. (Amended) A membrane according to [any preceding claim] claim 1, wherein said first conductive polymer is a copolymer comprising a first repeat unit which is selected from the following:

(a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

(c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and O represent 1;

(d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

(e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

(h) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

8. (Amended) A membrane according to [any preceding claim] claim 1,
wherein said first conductive polymer is a homopolymer having a repeat unit of
general formula



or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV* and/or

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V* wherein A, B, C and D independently represent 0 or 1.

9. (Amended) A membrane according to [any preceding claim] claim 1, wherein said first conductive polymer includes a biphenylene moiety.

10. (Amended) A membrane according to [any preceding claim] claim 1, wherein said first conductive polymer includes a -O--biphenylene-O-moiety.

11. (Amended) A membrane according to [any preceding claim] claim 1, wherein a film of said conductive polymer is laminated to the support material.

12. (Amended) A membrane according to [any of claims 1 to 10] claim 1, wherein the support material is porous and said conductive polymer is impregnated in the support material.

13. (Amended) A membrane according to [any preceding claim] claim 1, wherein said support material comprises a polymer having a moiety of formula I, II and/or III as described in [any preceding claim] claim 1 except that the polymer of the support material is either not sulphonated (or otherwise functionalised to provide ion-exchange sites) or is only sulphonated (or otherwise functionalised to provide ion—exchange sites) at or in the region of the surface of the support material.

14. (Amended) A membrane according to [any preceding claim] claim 1, wherein said support material is selected from the following homopolymers of formula IV as shown in claim 4:

- E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B

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represent 1

- E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero

- Ar represents a moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1.

- Ar represents a structure (i)*, E represents an oxygen atom, E' represents a direct link, m represents 0, A represents 1, B represents 0.

- Ar represents moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents zero, w represents 1, r represents 0, s represents 1 and A and B represent 1

- Ar represent moiety (iv); E represents a sulphur atom, m represents 0, E' represents a direct link and B represents 0;

or is selected from:

- a homopolymer of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; and is selected from:

- polysulphone for example comprising a homopolymer of formula V wherein E and E' represent oxygen atoms, m represents zero, C and D represent 1, z represents 1, G represents a direct link, v represents zero and Ar represents a moiety of structure:

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15. (Amended) A membrane according to [any preceding claim] claim 1, wherein said first conductive polymer has an equivalent weight (EW) of less than 800g/mol, preferably less than 500 g/mol.

17. (Amended) A fuel cell or electrolyser incorporating a composite membrane according to [any preceding claim] claim 1.

18. (Amended) A method of making a composite membrane according to [any of claims 1 to 16] claim 1, the method comprising causing a conductive polymer as described [in any of claims 1 to 16] above to be associated with a support material as described [in any of claims 1 to 16] above.

20. (Amended) A method according to claim 18 [or claim 19], wherein a first solvent formulation comprises a polar aprotic solvent in which a conductive polymer is provided and said support material is a material (e.g. a polyetheretherketone fabric or a polyetherketone microporous membrane) which is not soluble in said polar aprotic solvent, wherein the method includes a step of contacting said support material with said first solvent formulation.

21. (Amended) A method according to claim 18 [or claim 19], wherein said support material is a fabric and the method includes a step of contacting the fabric with a first solvent formulation comprising a first solvent and said conductive polymer, wherein said first solvent and said support material are

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selected so that the first solvent solubilizes a surface of the support material.

24. (Amended) A method according to claim 18 [or claim 19], the method including:

contacting said support material with a solvent formulation comprising a first solvent which solubilizes the support material; and

contacting the support material with a second solvent to cause phase inversion and render said support material porous.

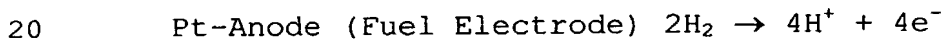
COMPOSITE ION-EXCHANGE MEMBRANES

This invention relates to a composite ion-exchange membrane and provides such a membrane per se and a method
5 of making such a membrane.

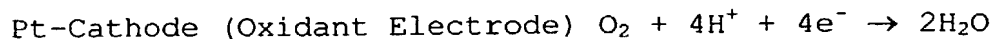
One type of known polymer electrolyte membrane fuel cell (PEMFC), shown schematically in Figure 1 of the accompanying diagrammatic drawings, may comprise a thin
10 sheet 2 of a hydrogen-ion conducting Polymer Electrolyte Membrane (PEM) sandwiched on both sides by a layer 4 of platinum catalyst and an electrode 6. The layers 2, 4, 6 make up a Membrane Electrode Assembly (MEA) of less than 1mm thickness.

15

In a PEMFC, hydrogen is introduced at the anode (fuel electrode) which results in the following electrochemical reaction:



The hydrogen ions migrate through the conducting PEM to the cathode. Simultaneously, an oxidant is introduced at the cathode (oxidant electrode) where the following
25 electrochemical reaction takes place:



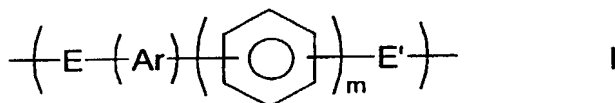
Thus, electrons and protons are consumed to produce
30 water and heat. Connecting the two electrodes through an external circuit causes an electrical current to flow in the circuit and withdraw electrical power from the cell.

The PEM 2 could comprise a single layer of ion-conducting material. However, in many cases, a single layer of material does not have satisfactory mechanical properties.

5

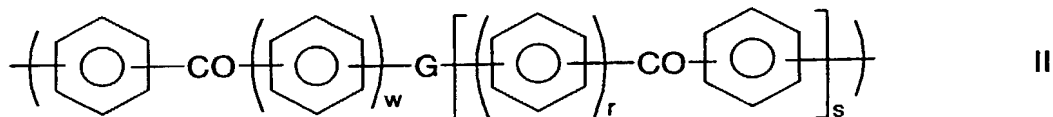
It is an object of the present invention to address the above described problem.

According to a first aspect of the invention, there is provided a composite membrane which includes a conductive polymer (i.e. an ion-conducting polymer) and a support material for the polymer, said polymer having a moiety of formula



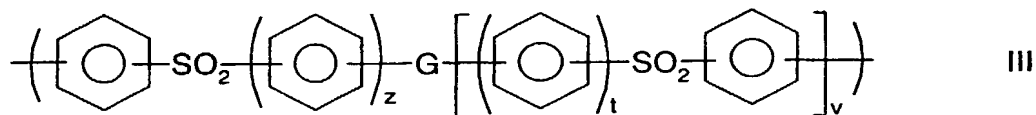
15

and/or a moiety of formula



and/or a moiety of formula

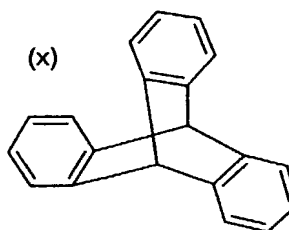
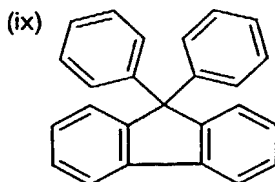
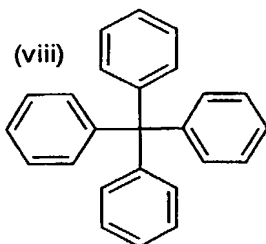
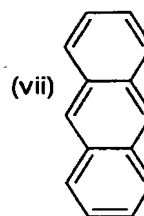
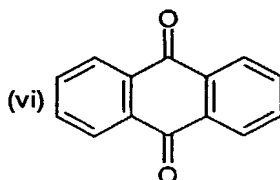
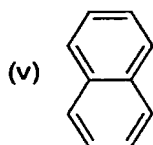
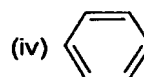
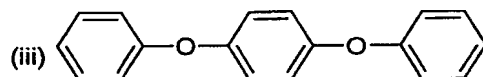
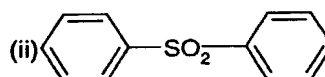
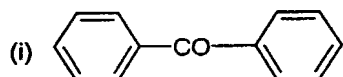
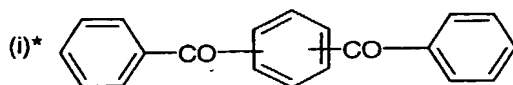
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wherein at least some of the units I, II and/or III are functionalized to provide ion exchange sites; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and

5 wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from

10 one of the following moieties (i)*, (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties



In (i)*, the middle phenyl may be 1,4- or 1,3-
5 substituted.

Preferably, said conductive polymer and said support material do not, together, define a homogenous mixture.

10 Suitably, to provide said ion exchange sites, said polymer is sulphonated, phosphorylated, carboxylated,

quaternary-aminoalkylated or chloromethylated, and optionally further modified to yield $-\text{CH}_2\text{PO}_3\text{H}_2$, $-\text{CH}_2\text{NR}_3^{20+}$ where R^{20} is an alkyl, or $-\text{CH}_2\text{NAr}_3^{x+}$ where Ar^x is an aromatic (arene), to provide a cation or anion exchange membrane.

5 Further still, the aromatic moiety may contain a hydroxyl group which can be readily elaborated by existing methods to generate $-\text{OSO}_3\text{H}$ and $-\text{OPO}_3\text{H}_2$ cationic exchange sites on the polymer. Ion exchange sites of the type stated may be provided as described in WO95/08581.

10

Preferably, said first conductive polymer is sulphonated. Preferably, the only ion-exchange sites of said first conductive polymer are sites which are sulphonated.

15

References to sulphonation include a reference to substitution with a group $-\text{SO}_3\text{M}$ wherein M stands for one or more elements selected with due consideration to ionic valencies from the following group: H, NR_4^{y+} , in which R^y stands for H, $\text{C}_1\text{-C}_4$ alkyl, or an alkali or alkaline earth metal or a metal of sub-group 8, preferably H, NR_4^+ , Na, K, Ca, Mg, Fe, and Pt. Preferably M represents H. Sulphonation of the type stated may be provided as described in WO96/29360.

25

Unless otherwise stated in this specification, a phenyl moiety may have 1,4- or 1,3-, especially 1,4-, linkages to moieties to which it is bonded.

30

Said polymer may include more than one different type of repeat unit of formula I; more than one different type of repeat unit of formula II; and more than one different type of repeat unit of formula III.

Said moieties I, II and III are suitably repeat units. In the polymer, units I, II and/or III are suitably bonded to one another - that is, with no other atoms or groups being bonded between units I, II, and III.

Where the phenyl moieties in units I, II or III are optionally substituted, they may be optionally substituted by one or more halogen, especially fluorine and chlorine, atoms or alkyl, cycloalkyl or phenyl groups. Preferred alkyl groups are C₁₋₁₀, especially C₁₋₄, alkyl groups. Preferred cycloalkyl groups include cyclohexyl and multicyclic groups, for example adamantyl. In some cases, the optional substituents may be used in the cross-linking of the polymer. For example, hydrocarbon optional substituents may be functionalised, for example sulphonated, to allow a cross-linking reaction to take place. Preferably, said phenyl moieties are unsubstituted.

Another group of optional substituents of the phenyl moieties in units I, II or III include alkyls, halogens, C_yF_{2y+1} where y is an integer greater than zero, O-R^q (where R^q is selected from the group consisting of alkyls, perfluoralkyls and aryls), CF=CF₂, CN, NO₂ and OH. Trifluormethylated phenyl moieties may be preferred in some circumstances.

Where said polymer is cross-linked, it is suitably cross-linked so as to improve its properties as a polymer electrolyte membrane, for example to reduce its swellability in water. Any suitable means may be used to effect cross-linking. For example, where E represents a sulphur atom, cross-linking between polymer chains may be

effected via sulphur atoms on respective chains. Alternatively, said polymer may be cross-linked via sulphonamide bridges as described in US 5 561 202. A further alternative is to effect cross-linking as described
5 in EP-A-0008895.

However, for polymers according to the invention described herein which are crystalline (which some are) there may be no need to effect cross-linking to produce a
10 material which can be used as a polymer electrolyte membrane. Such polymers may be easier to prepare than cross-linked polymers. Thus, said polymer of the inventions described herein may be crystalline. Preferably, said polymer is not optionally cross-linked as described.

15

Where w and/or z is/are greater than zero, the respective phenylene moieties may independently have 1,4- or 1,3-linkages to the other moieties in the repeat units of formulae II and/or III. Preferably, said phenylene
20 moieties have 1,4- linkages.

Preferably, the polymeric chain of the polymer does not include a -S- moiety. Preferably, G represents a direct link.

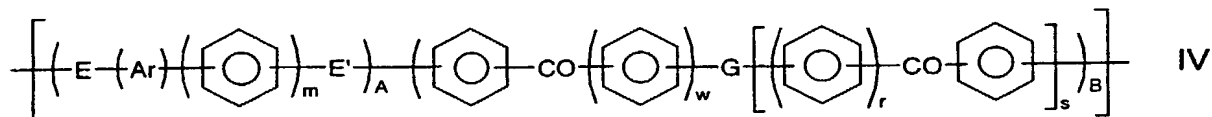
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Suitably, "a" represents the mole % of units of formula I in said polymer, suitably wherein each unit I is the same; "b" represents the mole % of units of formula II in said polymer, suitably wherein each unit II is the same;
30 and "c" represents the mole % of units of formula III in said polymer, suitably wherein each unit III is the same. Preferably, a is in the range 45-100, more preferably in the range 45-55, especially in the range 48-52.

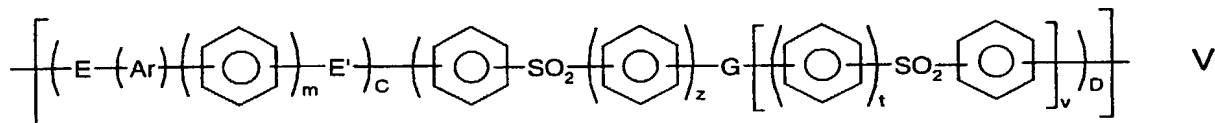
Preferably, the sum of b and c is in the range 0-55, more preferably in the range 45-55, especially in the range 48-52. Preferably, the ratio of a to the sum of b and c is in the range 0.9 to 1.1 and, more preferably, is about 1.

5 Suitably, the sum of a, b and c is at least 90, preferably at least 95, more preferably at least 99, especially about 100. Preferably, said polymer consists essentially of moieties I, II and/or III.

10 Said polymer may be a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



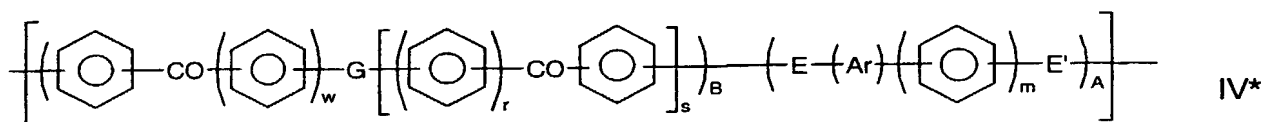
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or a random or block copolymer of at least two different units of IV and/or V

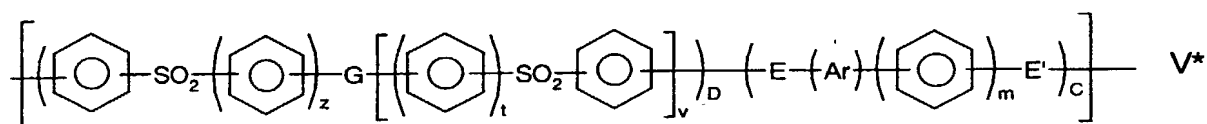
wherein A, B, C and D independently represent 0 or 1

20 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

As an alternative to a polymer comprising units IV and/or V discussed above, said polymer may be a homopolymer having a repeat unit of general formula



5 or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV* and/or V*, wherein A, B, C, and D independently represent 0 or 1 and E, E', G, Ar, m, r, s, t, v, w and z are as described in any statement herein.

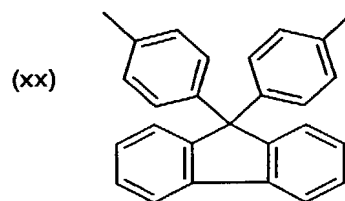
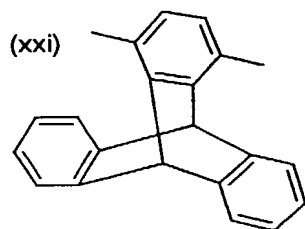
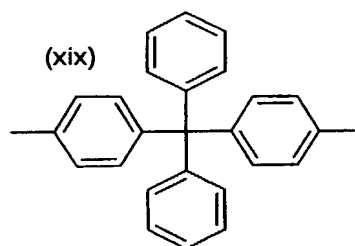
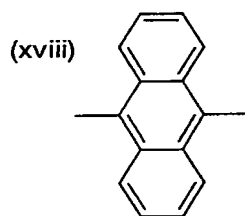
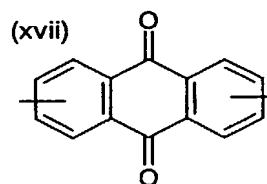
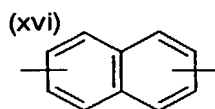
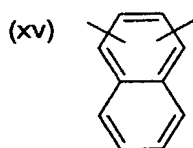
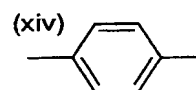
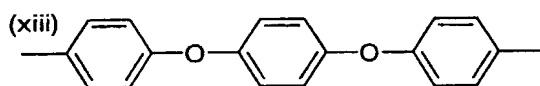
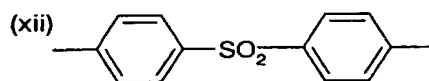
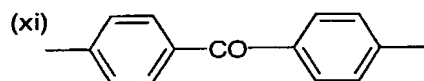
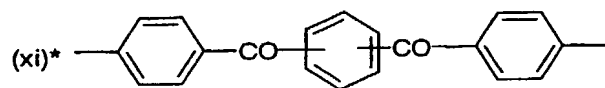
Preferably, m is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, r is in the range 0-3, more preferably 0-2, especially 0-1. Preferably t is in the range 0-3, more preferably 0-2, especially 0-1. Preferably, s is 0 or 1. Preferably v is 0 or 1. Preferably, w is 0 or 1. Preferably z is 0 or 1.

WO 01/19896

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10

Preferably Ar is selected from the following moieties
(xi)*, (xi) to (xxi):



In (xi)*, the middle phenyl may be 1,4- or 1,3-substituted.

5

One preferred class of polymers does not include any moieties of formula III, but suitably only includes moieties of formulae I and/or II. Where said polymer is a homopolymer or random or block copolymer as described, said homopolymer or copolymer suitably includes a repeat unit of general formula IV. Such a polymer may, in some embodiments, not include any repeat unit of general formula V.

Referring to formula IV, preferably, said polymer is not a polymer wherein: Ar represents moiety (iv), E and E' represent oxygen atoms, m represents zero, w represents 1, s represents zero, G represents a direct link and A and B represent 1; Ar represents moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents zero, w represents 1, r represents 0, s represents 1 and A and B represent 1; Ar represents moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m

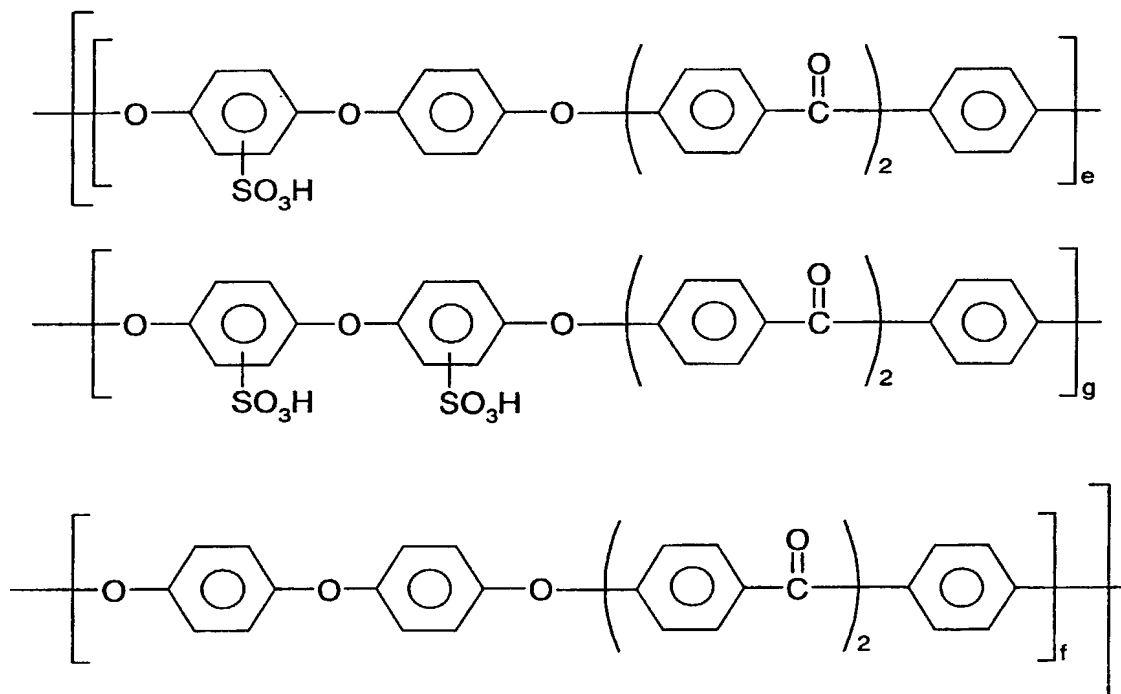
where

e is from 0.2 to 1,

f is from 0 to 0.8, and

e + f = 1

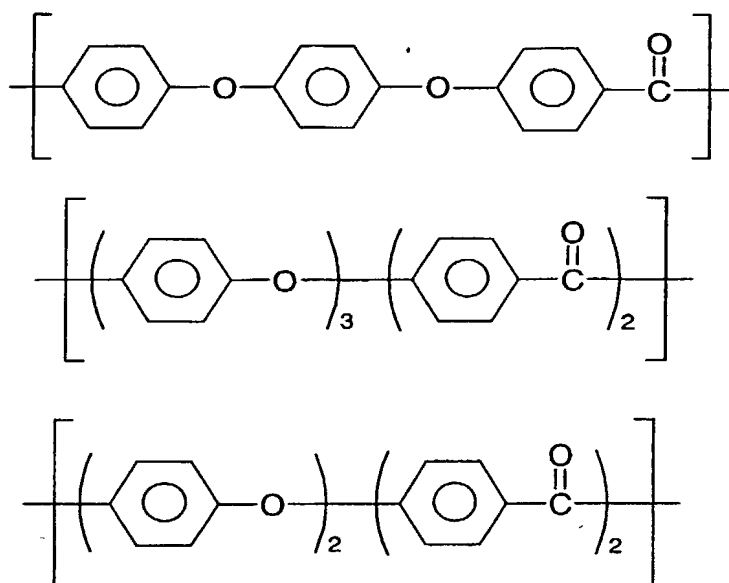
Preferably, said polymer does not conform to the
5 formula



in which e is a number from 0 to 1, g is a number from
0 to 1, f is a number from 0 to 0.5, and the sum e + f + g
10 = 1.

Preferably, said polymer is not a copolymer built up
from at least two different units of formulae:

15



Suitable moieties Ar are moieties (i), (ii), (iv) and (v) and, of these, moieties (i), (ii) and (iv) are preferred. Preferred moieties Ar are moieties (xi), (xii), (xiv), (xv) and (xvi) and, of these, moieties (xi), (xii) and (xiv) are especially preferred. Another preferred moiety is moiety (v), especially, moiety (xvi). In relation, in particular to the alternative polymers comprising units IV* and/or V*, preferred Ar moieties are (v) and, especially, (xvi).

Preferred polymers include an electron-rich, relatively non-deactivated, easily sulphonatable unit, for example a multi-phenylene moiety or a fused-rings aromatic moiety, such as naphthalene. Such an easy to sulphonate unit may be sulphonated under relatively mild conditions to introduce two sulphonate groups per unit. Thus, preferred polymers may have at least 10π electrons in a delocalized aromatic moiety. The number of π electrons may be 12 or less.

Preferred polymers include a biphenylene moiety. Other preferred polymers include a naphthalene moiety. Preferred polymers include said electron rich, non-deactivated, easily sulphonatable unit bonded to two oxygen atoms.

5 Especially preferred polymers include a -O-biphenylene-O-moiety. Other especially preferred polymers include a -O-naphthalene-O- moiety.

Preferred polymers include a first type of moiety which is relatively difficult to sulphonate and a second type of moiety which is relatively easy to sulphonate. For example, said second moiety may be sulphonatable using the relatively mild method described in Example 2 hereinafter, whereas the first moiety may be substantially non-sulphonatable in such a method. The use of the method of Example 2 may be advantageous over currently used methods which use oleum. A preferred second said moiety includes a moiety $-Ph_n-$ wherein n is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen.

10 is relatively difficult to sulphonate and a second type of moiety which is relatively easy to sulphonate. For example, said second moiety may be sulphonatable using the relatively mild method described in Example 2 hereinafter, whereas the first moiety may be substantially non-sulphonatable in such a method. The use of the method of Example 2 may be advantageous over currently used methods which use oleum. A preferred second said moiety includes a moiety $-Ph_n-$ wherein n is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen.

15 sulphonatable in such a method. The use of the method of Example 2 may be advantageous over currently used methods which use oleum. A preferred second said moiety includes a moiety $-Ph_n-$ wherein n is an integer of at least 2. Said moiety is preferably bound to at least one ether oxygen.

20 Especially preferred is the case wherein said moiety is $-O-Ph_n-O-$ where said ether groups are para to the Ph-Ph bond.

Preferred polymers are copolymers comprising (preferably consisting essentially of) a first repeat unit which is selected from the following:

25 which is selected from the following:

(a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;

30 represents 1 and A and B represent 1;

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety

(h) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a

moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

Other second units which may form copolymers with any of said first repeat units (a) to (e) above include: a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, w represents 1, s represents 0, A and B represent 1; or a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (v), m represents 0, z represents 1, v represents 0, C and D represent 1.

Preferred polymers for some situations may comprise first units selected from (a), (b), (c) and (e) and second units selected from (f), (g), (h) or (i). A polymer comprising units (d) and (h) may also be preferred.

More preferred polymers are copolymers having a first repeat unit selected from those described above, especially repeat units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h).

Preferred polymers having repeat unit(s) of formulae IV* and V* may include: a unit of formula IV* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, w, s and m represent 0, A and B represent 1; and/or a

repeat unit of formula V* wherein Ar represents a moiety of structure (v), E represents a direct link, E' represents an oxygen atom, G represents a direct link, z, v and m represent 0, C and D represent 1.

5

Said polymers having repeat units IV* and V* may include any of repeat units (a) to (i) described above.

In some situations, polymers which include at least one repeat unit of formula IV or formula IV* may be preferred.

10

Copolymers may be prepared having one or more first repeat units and one or more of said second repeat units.

15

Where said polymer is a copolymer as described, the mole% of co-monomer units, for example said first and second repeat units described above, may be varied to vary the solubility of the polymer in solvents, for example in organic solvents which may be used in the preparation of films and/or membranes from the polymers and/or in other solvents, especially water.

20

Preferred polymers suitably have a solubility of at least 10% w/v, (especially at least 10% w/w) preferably a solubility in the range 10 to 30% w/v (especially in the range 10 to 30% w/w) in a polar aprotic solvent, for example NMP, DMSO or DMF. Preferred polymers are substantially insoluble in boiling water.

25

30

First units of the type described above (with the exception of units (a) and (c)) may be relatively difficult to sulphonate, whereas second units of the type described may be easier to sulphonate.

Where a phenyl moiety is sulphonated, it may only be mono-sulphonated. However, in some situations it may be possible to effect bi- or multi-sulphonation.

5

In general terms, where a said polymer includes a -O-phenyl-O- moiety, up to 100 mole% of the phenyl moieties may be sulphonated. Where a said polymer includes a -O-biphenylene-O- moiety, up to 100 mole% of the phenyl
10 moieties may be sulphonated. It is believed to be possible to sulphonate relatively easily -O-(phenyl)_n-O- moieties wherein n is an integer, suitably 1-3, at up to 100 mole%. Moieties of formula -O-(phenyl)_n-CO- or -O-(phenyl)_n-SO₂- may also be sulphonated at up to 100 mole% but more
15 vigorous conditions may be required. Moieties of formulae -CO-(phenyl)_n-CO- and -SO₂-(phenyl)_n-SO₂- are more difficult to sulphonate and may be sulphonated to a level less than 100 mole% or not at all under some sulphonation conditions.

20 The glass transition temperature (T_g) of said polymer may be at least 144°C, suitably at least 150°C, preferably at least 154°C, more preferably at least 160°C, especially at least 164°C. In some cases, the T_g may be at least 170°C, or at least 190°C or greater than 250°C or even
25 300°C.

Said polymer may have an inherent viscosity (IV) of at least 0.1, suitably at least 0.3, preferably at least 0.4, more preferably at least 0.6, especially at least 0.7
30 (which corresponds to a reduced viscosity (RV) of least 0.8) wherein RV is measured at 25°C on a solution of the polymer in concentrated sulphuric acid of density 1.84gcm⁻³, said solution containing 1g of polymer per 100cm⁻³ of

solution. IV is measured at 25°C on a solution of polymer in concentrated sulphuric acid of density 1.84gcm³, said solution containing 0.1g of polymer per 100cm³ of solution.

5 The measurements of both RV and IV both suitably employ a viscometer having a solvent flow time of approximately 2 minutes.

10 The main peak of the melting endotherm (T_m) for said polymer (if crystalline) may be at least 300°C.

15 In general terms, said composite membrane is preferably substantially stable when used as a PEM in a fuel cell. Thus, it suitably has high resistance to oxidation, reduction and hydrolysis and has very low permeability to reactants in the fuel cell. Preferably, however, it has a high proton conductivity. Furthermore, it suitably has high mechanical strength and is capable of being bonded to other components which make up a membrane electrode
20 assembly.

25 Said polymer may comprise a film, suitably having a thickness of less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05 mm. The film may have a thickness of at least 5µm.

30 Said polymer electrolyte membrane may comprise one or more layers wherein, suitably, at least one layer comprises a film of said polymer. Said membrane may have a thickness of at least 5µm and, suitably, less than 1mm, preferably less than 0.5mm, more preferably less than 0.1mm, especially less than 0.05mm.

Said support material suitably imports mechanical strength and dimensional stability to the composite membrane. The polymer may be associated with the support material to form a composite membrane in a variety of ways.

5 For example, an unsupported conductive polymer film can be preformed and laminated to the support material. Alternatively, (and preferably) the support material may be porous and a solution of the conductive polymer can be impregnated into the support material. Said support

10 material may comprise or consist essentially of an optionally-substituted polyolefin. Preferred polyolefins are optionally-substituted polyethylene and polypropylene. In one embodiment, the support material may comprise, or preferably consist essentially of, polytetrafluoroethylene

15 or surface modified polytetrafluoroethylene, suitably provided as a porous film. Such a support material may be as described and used in accordance with the teachings of WO97/25369 and WO96/28242, the contents of which are incorporated herein by reference. Suitably, the support

20 material has a porous microstructure of polymeric fibrils and is impregnated with said polymer throughout the material, preferably so as to render an interior volume of the membrane substantially occlusive.

25 Said support material may be made of any polymer described herein for said conductive polymer except that the polymer of said support material is either not sulphonated or otherwise functionalized to provide ion-exchange sites or is only sulphonated (or otherwise

30 functionalized to provide ion-exchange sites) at or in the region of the surface of the support material - that is, functionalisation of said support material is greater at the surface than in interior regions thereof. The EW of

said support material may be greater than 2000. Thus, said support material may comprise a polymer having moieties I, II and/or III or a homopolymer or copolymer comprising units IV and/or V.

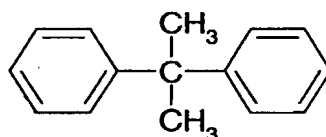
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Preferably said support material is selected from the following homopolymers of formula IV:

- 10 - E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1
- E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m
15 represents zero, A represents 1, B represents zero
- Ar represents a moiety (iv), E and E' represent oxygen atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and
20 B represent 1.
- Ar represents a structure (i)*, E represents an oxygen atom, E' represents a direct link, m represents 0, A represents 1, B represents 0.
25
- Ar represents moiety (i), E and E' represent oxygen atoms, G represents a direct link, m represents zero, w represents 1, r represents 0, s represents 1 and A and
30 B represent 1

- Ar represent moiety (iv), E represents a sulphur atom, m represents 0, E' represents a direct link and B represents 0 and is selected from:
- 5 - a homopolymer of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; and is selected from:
- polysulphone for example comprising a homopolymer of
10 formula V wherein E and E' represent oxygen atoms, m represents zero, C and D represent 1, z represents 1, G represents a direct link, v represents zero and Ar represents a moiety of structure:

15



Blends of the abovementioned materials may be used.

- 20 Said support material may be any support material described in WO99/10165 the content of which is incorporated herein, as regards said support materials.

Said support material is preferably impregnated with
25 said conductive polymer. Said support material is preferably porous and, suitably, said conductive polymer is arranged in pores of said support material, preferably so as to render an interior volume of the support material substantially occlusive.

30

Preferably, said support material and said conductive polymer are in intimate contact. Whilst the two materials preferably do not together define a homogeneous material, the support material and conductive polymer preferably intermingle (as would happen if, for example a surface of the support material was dissolved and contacted with said conductive material) in a boundary region between the two materials.

The use of support material as described may allow polymers of lower equivalent weights (EW) (for example less than 800g/mol, less than 700 g/mol, less than 600 g/mol, 25 suitably less than 500 g/mol, preferably less than 450 g/mol or even less than 400 g/mol or 370 g/mol) or relatively inflexible and/or brittle polymers to be used as said conductive polymer in said composite membrane.

30 The composite membrane suitably includes a catalyst material (preferably a layer of a catalyst material) which is suitably a platinum catalyst (i.e. platinum containing) or a mixture of platinum and ruthenium, on both sides of

the support material/conductive polymer arrangement described. Electrodes may be provided outside the catalyst material.

5 It may be preferable for each phenyl group in a conductive polymer (e.g. a sulphonated polymer) as described to be deactivated by being bonded directly to an electron withdrawing group, for example a sulphonated group, a sulphone group or a ketone group.

10

According to a second aspect of the invention, there is provided a composite membrane which includes a conductive polymer and a support material for the polymer, wherein said polymer includes: polyaryletherketone and/or
15 polyarylethersulphone units; and units of formula $-O-Ph_n-O-$ (XX) wherein Ph represents a phenyl group and n represents an integer of 2 or greater and wherein Ph groups of units (XX) are sulphonated.

20 Preferably, each phenyl group of moiety Ph_n is sulphonated, preferably mono-sulphonated. About 100 mole% of such phenyl groups may be sulphonated as described.

Preferably, $-OPhCO-$ and/or $-OPhSO_2-$ moieties of said
25 polymer are sulphonated to a lesser extent than the phenyl groups of moiety Ph_n . Moieties $-OPhCO-$ and $-OPhSO_2-$ may be substantially non-sulphonated.

In one embodiment, said polymer may include no ketone
30 linkages and may have an equivalent weight of more than 900. Nonetheless, it has been found, surprisingly, that such polymers are still conducting.

Said composite membrane may be for a fuel cell or an electrolyser.

In addition to the utility of the composite membranes described herein as ion-exchange membranes for electrochemical fuel cells, the following further utilities are also contemplated:

1. Proton exchange membrane based water electrolysis, which involves a reverse chemical reaction to that employed in hydrogen/oxygen electrochemical fuel cells.
2. Chloralkali electrolysis, typically involving the electrolysis of a brine solution to produce chlorine and sodium hydroxide, with hydrogen as a by-product.
3. Electrode separators in conventional batteries due to the chemical inertness and high electrical conductivity of the composite membranes.
4. Ion-selective electrodes, particularly those used for the potentiometric determination of a specific ion such as Ca^{2+} , Na^+ , K^+ and like ions. The composite membrane could also be employed as the sensor material for humidity sensors, as the electrical conductivity of an ion exchange membrane varies with humidity.
5. Ion-exchange material for separations by ion-exchange chromatography. Typical such applications are deionization and desalination of water (for example, the purification of heavy metal contaminated water), ion separations (for example, rare-earth metal ions, trans-uranium elements), and the removal of interfering ionic species.
6. Ion-exchange membranes employed in analytical preconcentration techniques (Donnan Dialysis). This technique is typically employed in analytical chemical

processes to concentrate dilute ionic species to be analysed.

7. Ion-exchange membranes in electrodialysis, in which membranes are employed to separate components of an ionic solution under the driving force of an electrical current. Electrolysis applications include the industrial-scale desalination of brackish water, preparation of boiler feed make-up and chemical process water, de-ashing of sugar solutions, deacidification of citrus juices, separation of amino acids, and the like.
8. Membranes in dialysis applications, in which solutes diffuse from one side of the membrane (the feed side) to the other side according to their concentration gradient. Separation between solutes is obtained as a result of differences in diffusion rates across the membrane arising from differences in molecular size. Such applications include hemodialysis (artificial kidneys) and the removal of alcohol from beer.
9. Membranes in gas separation (gas permeation) and pervaporation (liquid permeation) techniques.
10. Bipolar membranes employed in water splitting and subsequently in the recovery of acids and bases from waste water solutions.

The invention extends to the use of a polymer which includes relatively easy to sulphonate units and relatively difficult to sulphonate units in the preparation of a conductive polymer for a composite membrane as described herein.

30

The conductive polymer described herein may include a blend of polymers, at least one of which is a polymer described according to the invention described herein.

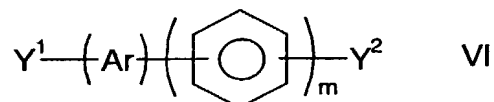
Suitably the conductive polymers herein are blended with 0-40wt%, preferably 0-20wt%, more preferably 0-10wt%, especially 0-5wt% of other polymeric materials. Preferably, however, a blend of polymers is not provided.

5

According to a third aspect of the invention, there is provided a fuel cell or an electrolyser (especially a fuel cell) incorporating a polymer electrolyte membrane according to the first or second aspects. The fuel cell may
10 be a hydrogen or direct methanol fuel cell.

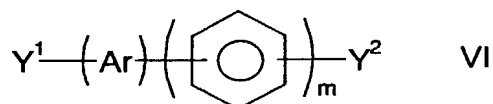
Polymers having units I, II, III, IV, IV*, V and/or V* may be prepared by:

15 (a) polycondensing a compound of general formula

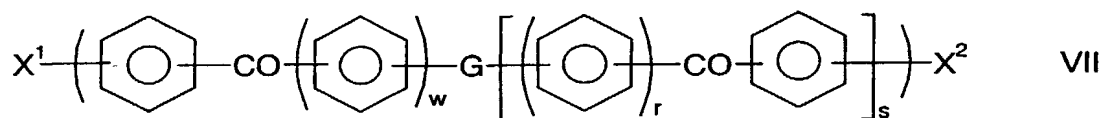


with itself wherein Y^1 represents a halogen atom or a group -EH and Y^2 represents a halogen atom or, if Y^1
20 represents a halogen atom, Y^2 represents a group E'H; or

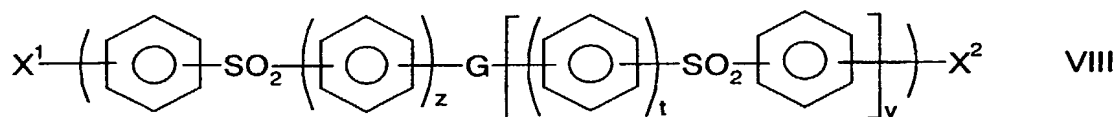
(b) polycondensing a compound of general formula



with a compound of formula



and/or with a compound of formula



5

wherein Y^1 represents a halogen atom or a group $-EH$ (or $-E'H$ if appropriate) and X^1 represents the other one of a halogen atom or group $-EH$ (or $-E'H$ if appropriate) and Y^2 represents a halogen atom or a group $-E'H$ and X^2 represents the other one of a halogen atom or a group $-E'H$ (or $-EH$ if appropriate).

10

(c) optionally copolymerizing a product of a process as described in paragraph (a) with a product of a process as described in paragraph (b);

15

wherein the phenyl moieties of units VI, VII and/or VIII are optionally substituted; the compounds VI, VII and/or VIII are optionally sulphonated; and Ar, m, w, r, s, z, t, v, G, E and E' are as described above except that E and E' do not represent a direct link;

20

the process also optionally comprising sulphonating and/or cross-linking a product of the reaction described in paragraphs (a), (b) and/or (c) to prepare said polymer.

25

In some situations, the polymer prepared, more particularly phenyl groups thereof, may be optionally substituted with the groups hereinabove described after
5 polymer formation.

Preferably, where Y^1 , Y^2 , X^1 and/or X^2 represent a halogen, especially a fluorine, atom, an activating group, especially a carbonyl or sulphone group, is arranged ortho-
10 or para- to the halogen atom.

Preferred halogen atoms are fluorine and chlorine atoms, with fluorine atoms being especially preferred. Preferably, halogen atoms are arranged meta- or para- to
15 activating groups, especially carbonyl groups.

Wherein the process described in paragraph (a) is carried out, preferably one of Y^1 and Y^2 represents a fluorine atom and the other represents an hydroxy group.
20 More preferably in this case, Y^1 represents a fluorine atom and Y^2 represents an hydroxy group. Advantageously, the process described in paragraph (a) may be used when Ar represents a moiety of structure (i) and m represents 1.

25 When a process described in paragraph (b) is carried out, preferably, Y^1 and Y^2 each represent an hydroxy group. Preferably, X^1 and X^2 each represent a halogen atom, suitably the same halogen atom.

30 Compounds of general formula VI, VII and VIII are commercially available (eg from Aldrich U.K) and/or may be prepared by standard techniques, generally involving Friedel-Crafts reactions, followed by appropriate

derivatisation of functional groups. The preparations of some of the monomers described herein are described in P M Hergenrother, B J Jensen and S J Havens, Polymer 29, 358 (1988), H R Kricheldorf and U Delius, Macromolecules 22, 517 (1989) and P A Staniland, Bull, Soc, Chem, Belg., 98 (9-10), 667 (1989).

Where compounds VI, VII and/or VIII are sulphonated, compounds of formulas VI, VII and/or VIII which are not sulphonated may be prepared and such compounds may be sulphonated prior to said polycondensation reaction.

Sulphonation as described herein may be carried out in concentrated sulphuric acid (suitably at least 96% w/w. preferably at least 97%w/w, more preferably at least 98%w/w; and preferably less than 98.5%w/w) at an elevated temperature. For example, dried polymer may be contacted with sulphuric acid and heated with stirring at a temperature of greater than 40°C, preferably greater than 55°C, for at least one hour, preferably at least two hours, more preferably about three hours. The desired product may be caused to precipitate, suitably by contact with cooled water, and isolated by standard techniques. Sulphonation may also be effected as described in US5362836 and/or EP0041780.

According to another aspect of the invention, there is provided a method of making a composite membrane as described herein, the method comprising causing a conductive polymer as described herein to be associated with a support material as described herein.

The conductive polymer may be associated with the support material in a variety of ways. The method may involve laminating conducting polymer and support material together. Preferably, however, the method involves
 5 impregnating porous support material with said conductive polymer.

Said porous support material may be a fabric or a microporous membrane.

10

Where said porous support material is a fabric, the method may include a step of contacting the fabric with a first solvent formulation comprising a first solvent and a conductive polymer, wherein the conductive polymer is
 15 preferably dissolved in the first solvent. Said fabric may, therefore, be impregnated with said formulation. Thereafter, said first solvent may be removed, leaving said conductive polymer in pores of said fabric.

20

Said first solvent and said porous support material may be selected so that said first solvent solubilises, to some degree, a surface of the support material. Said first solvent may be capable of dissolving the support material to a level of at least 5wt%. This may improve
 25 contact between the conductive polymer and said support material. Optionally, said first solvent may be capable of functionalizing (e.g. sulphonating) said support material to provide ion-exchange site on a surface thereof as hereinbefore described.

30

Said first solvent may be a polar aprotic solvent, for example NMP, or may be a protic solvent. A polar aprotic solvent may not be capable of solubilising said porous

Where said support is a microporous membrane, preparation of the membrane may include a step of contacting a support material as described herein with a solvent formulation comprising said first solvent. Said first solvent preferably solubilizes the support material. Subsequently, the method preferably includes the step of contacting the support material with a second solvent.

Said second solvent is preferably arranged to cause phase inversion. Phase inversion suitably results in said support material being rendered porous. Said second solvent is preferably a non-solvent for said support material. Preferred second solvents are aqueous; especially preferred is water.

Said microporous support material is preferably contacted with said conductive polymer so that said polymer penetrates into pores formed in said porous material. Said conductive polymer may be provided in a third solvent, thereby to penetrate pores in said support material. Said third solvent is preferably a polar aprotic solvent. NMP is a suitable solvent. Thereafter, the third solvent is evaporated.

Said third solvent may have the same identity as said first solvent described above. Said conductive material may be contacted with said support material in the first solvent. Phase inversion may then be caused as described above which results in said conductive polymer being deposited in the pores formed by the phase inversion. After deposition of said conductive polymer in pores, as described above, the arrangement may be post-treated, suitably so as to produce a substantially continuous film of said conductive polymer on the support material. Post-treatment may include the step of contacting the composite membrane which comprises conductive polymer in pores of said support material with a third solvent in which said conductive polymer is relatively soluble and said support material is substantially insoluble. This may cause some dissolution of the conductive polymer in the pores resulting in film formation by coalescence of material

between pores. Optionally, a said conductive polymer may be provided in said third solvent, thereby to penetrate pores in said support material. Said third solvent is preferably a polar aprotic solvent. NMP is a suitable solvent. Thereafter, the third solvent is evaporated.

The method may include a subsequent step of associating a catalyst material with the composite membrane prepared as described.

A said composite membrane described herein may be used in fuel cells or electrolyzers and, accordingly, the invention extends to a fuel cell or electrolyser incorporating a composite membrane as described.

Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein.

Specific embodiments of the invention will now be described, by way of example, with reference to figure 1 which is a schematic representation of a polymer electrolyte membrane fuel cell.

The abbreviation NMP referred to means N-methylpyrrolidone.

PEEKTM and PEKTM are trade marks of Victrex Plc for polyetheretherketone and polyetherketone respectively.

In the specification sulphonated polyether(biphenyl)etherketone is referred to as SPEDEK;

Example 2

The polymer of Example 1 was sulphonated by stirring each polymer in 98% sulphuric acid (3.84g polymer/100g sulphuric acid) for 21 hours at 50°C. Thereafter, the reaction solution was allowed to drip into stirred
5 deionised water. Sulphonated polymer precipitated as free-flowing beads. Recovery was by filtration, followed by washing with deionised water until the pH was neutral and subsequent drying. In general, ¹H nmr in DMSO-d₆ confirmed that 100 mole% of the biphenyl units had
10 sulphonated, giving one sulphonic acid group, ortho to the ether linkage, on each of the two aromatic rings comprising the biphenyl unit, giving an Equivalent Weight of 583.

15 Example 3

Membranes were produced from the polymer from Example 2 after sulphonation as described in Example 2 by dissolving the polymer in N-methylpyrrolidone (NMP) at a
20 concentration of 15% w/w. The homogeneous solution was cast onto clean glass plates and then drawn down to give 400 micron films, using a stainless steel Gardner Knife. Evaporation at 100°C under vacuum for 24 hours produced membranes of mean thickness 40 microns.

25

Example 4

The substrate, a piece of PEEK™ fabric having a thickness of 70µm and weight/unit area of 1.7x10⁻³g.cm⁻²
30 was clamped in a 10 cm diameter circular frame and immersed in a 15% (w/w) solution of SPEDEK/PEKES(1:1:5) prepared in Example 2 in NMP. The wetted substrate was placed in vacuum oven at 105°C for 1.5 hrs to remove the

	Hydrogen Pressure	3Barg
	Air Pressure	3Barg
	Hydrogen Stoichiometry	1.5
30	Air Stoichiometry	3
	Cell Temperature	50°C
	Current Density	0.7Acm ⁻²

A 10% (w/w) solution of PEK™ (Grade P22, obtained from Victrex Plc, UK, having a Melt Viscosity of 0.22 kN sm⁻²)

in 98% sulphuric acid was cast onto a glass plate to produce a 100 µm wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP to produce a wet thickness of the solution of 250 µm, followed by drying for 20 hours at 105 °C producing a membrane of mean thickness 50 microns. The weight ratio of ion-conducting membrane to PEKTM microporous membrane was 80:20. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite membrane was strong and flexible.

Example 9

A 5cm x 5cm x 50 microns sample of membrane from Example 8 and a 5cm x 5cm x 40 microns sample of the membrane from Example 3 were separately immersed in boiling deionised water (500 ml) for 60 mins, removed and dried quickly with lint-free paper to remove surface water, weighed, dried in an oven at 50°C for 1 day, allowed to cool to ambient temperature in a desiccator then weighed quickly. The % water-uptakes were 132% and 520% for the reinforced composite membrane and unreinforced membrane respectively, as calculated below.

$$\% \text{ Water-uptake} = \frac{\text{Wet Weight} - \text{Dry Weight}}{\text{Dry Weight}} \times 100$$

Example 10

A 10% (w/w) solution of PES was dissolved in 98% sulphuric acid and was cast onto a glass plate to produce
5 a 100 μm wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP to produce a wet
10 thickness of the solution of 250 μm , followed by drying for 20 hours at 105°C. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite membrane was strong and flexible.

15

Example 11

The substrate, a 10 cm by 10 cm piece of PTFE fabric was clamped to a glass plate, impregnated with a 5% (w/w)
20 solution of the SPEDEK/PEKES polymer prepared in Example 2 in NMP/methanol (30:70; w/w) and immersed in de-ionized water. The composite membrane was dried then coated using a Doctor Blade with a coating of a 5% (w/w) solution of SPEDEK/PEKES polymer prepared in Example 2 in NMP/methanol
25 (30:70; w/w), to 250 μm wet thickness and dried. The coating procedure was repeated. Compared to the unreinforced membrane described in Example 3 which was highly swollen and fragile after immersion in boiling water for 1 hour, the composite membrane was strong and
30 flexible.

Example 12

A 7% (w/w) solution of Victrex ® PEEK™ (Grade 450G, obtained from Victrex Plc, UK, having a Melt Viscosity of 0.45kNsm⁻²) in methanesulphonic acid was cast onto a glass plate to produce a 100 µm wet thickness coating. The plate was immersed in deionized water, removed, dried under vacuum at 105°C, thereby producing a microporous membrane. This membrane was then impregnated with a 15% (w/w) solution of SPEDEK/PEKES prepared in Example 2 in NMP to produce a wet thickness of the solution of 250 µm, followed by drying for 20 hours at 105 °C. Compared to the wet unreinforced membrane described in Example 3 which was highly swollen and fragile, the wet composite membrane was strong and flexible.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

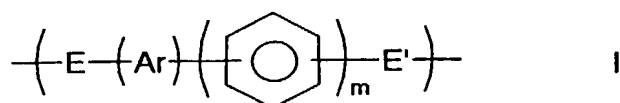
All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise,

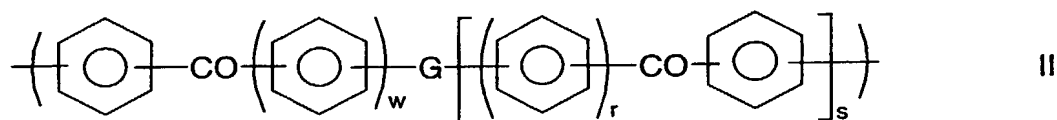
The invention is not restricted to the details of the foregoing embodiment(s). The invention extend to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A composite membrane which includes a conductive polymer and a support material for the polymer, said
 5 polymer having a moiety of formula

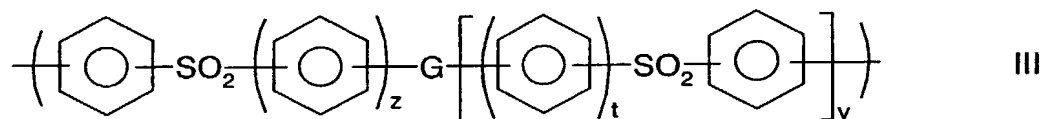


and/or a moiety of formula



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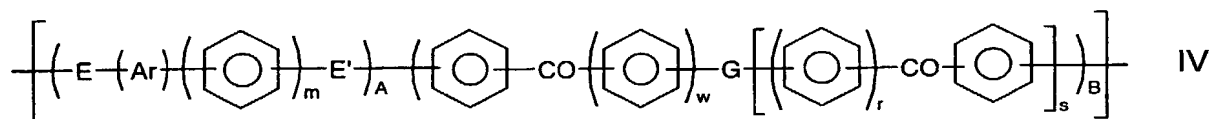
and/or a moiety of formula



- wherein at least some of the units I, II and/or III are
 15 functionalized to provide ion exchange sites; wherein the
 phenyl moieties in units I, II, and III are independently
 optionally substituted and optionally cross-linked; and
 wherein m, r, s, t, v, w and z independently represent zero or a
 positive integer, E and E' independently represent an
 20 oxygen or a sulphur atom or a direct link, G represents an
 oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety

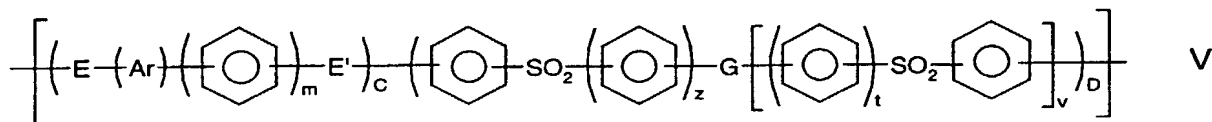
3. A membrane according to claim 1 or claim 2, wherein said first conductive polymer is crystalline.

4. A membrane according to any preceding claim, wherein
5 said polymer is a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula

10



or a random or block copolymer of at least two different units of IV and/or V

15 wherein A, B, C and D independently represent 0 or 1.

5. A membrane according to any preceding claim, wherein said first conductive polymer includes at least some ketone moieties in the polymeric chain.

20

6. A membrane according to any preceding claim, wherein said first conductive polymer is a copolymer comprising a first repeat unit which is selected from the following:

25 (a) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a

moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1;

(b) a unit of formula IV wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero;

(c) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1 and C and D represent 1;

(d) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; or

(e) a unit of formula V wherein E and E' represents an oxygen atom, Ar represents a structure (i), m represents 0, C represents 1, Z represents 1, G represents a direct link, v represents 0 and D represents 1;

and a second repeat unit which is selected from the following:

(f) a unit of formula IV wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, w represents 1, s represents zero, A and B represent 1;

(g) a unit of formula IV wherein E represents an oxygen atom, E' is a direct link, G represents a direct link, Ar

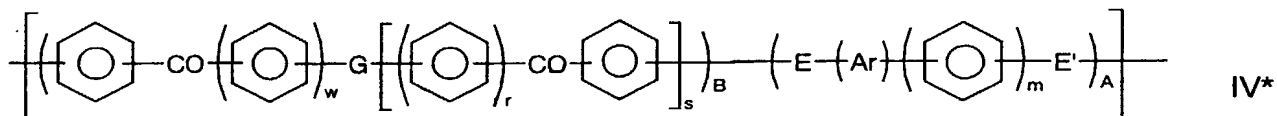
represents a moiety of structure (iv), m and s represent zero, w represent 1, A and B represent 1;

(h) a unit of formula V wherein E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m represents 1, z represents 1, v represents 0, C and D represent 1; and

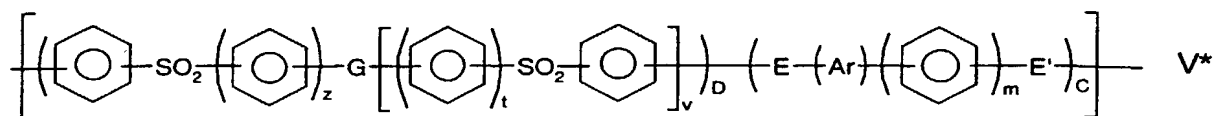
(i) a unit of formula V wherein E represents an oxygen atom, E' represents a direct link, G represents a direct link, Ar represents a moiety of structure (iv), m and v represent zero, z represents 1, C and D represent 1;

7. A membrane according to claim 6, wherein said first conductive polymer includes a first repeat unit selected from repeat units (b), (d) or (e) in combination with a second repeat unit selected from units (f) or (h).

8. A membrane according to any preceding claim, wherein said first conductive polymer is a homopolymer having a repeat unit of general formula



or a homopolymer having a repeat unit of general formula



or a random or block copolymer of at least two different units of IV* and/or V* wherein A, B, C and D independently represent 0 or 1.

5

9. A membrane according to any preceding claim, wherein said first conductive polymer includes a biphenylene moiety.

10. A membrane according to any preceding claim, wherein said first conductive polymer includes a -O-biphenylene-O-moiety.

11. A membrane according to any preceding claim, wherein a film of said conductive polymer is laminated to the support material.

12. A membrane according to any of claims 1 to 10, wherein the support material is porous and said conductive polymer is impregnated in the support material.

13. A membrane according to any preceding claim, wherein said support material comprises a polymer having a moiety of formula I, II and/or III as described in any preceding claim except that the polymer of the support material is either not sulphonated (or otherwise functionalised to provide ion-exchange sites) or is only sulphonated (or otherwise functionalised to provide ion-exchange sites) at or in the region of the surface of the support material.

14. A membrane according to any preceding claim, wherein said support material is selected from the following homopolymers of formula IV as shown in claim 4:

5

- E and E' represent oxygen atoms, G represents a direct link, Ar represents a moiety of structure (iv), m and s represent zero, w represents 1 and A and B represent 1

10 - E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (i), m represents zero, A represents 1, B represents zero

- Ar represents a moiety (iv), E and E' represent oxygen
15 atoms, G represents a direct link, m represents 0, w represents 0, s represents 1, r represents 1 and A and B represent 1.

- Ar represents a structure (i)*, E represents an oxygen
20 atom, E' represents a direct link, m represents 0, A represents 1, B represents 0.

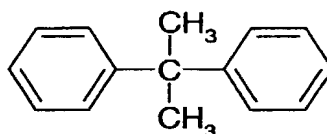
- Ar represents moiety (i), E and E' represent oxygen
atoms, G represents a direct link, m represents zero, w
25 represents 1, r represents 0, s represents 1 and A and B represent 1

- Ar represent moiety (iv), E represents a sulphur atom,
m represents 0, E' represents a direct link and B
30 represents 0;

or is selected from:

- a homopolymer of formula V wherein E represents an oxygen atom, E' represents a direct link, Ar represents a moiety of structure (ii), m represents 0, C represents 1, D represents 0; and is selected from:
- 5 - polysulphone for example comprising a homopolymer of formula V wherein E and E' represent oxygen atoms, m represents zero, C and D represent 1, z represents 1, G represents a direct link, v represents zero and Ar represents a moiety of structure:

10



- 15 15. A membrane according to any preceding claim, wherein said first conductive polymer has an equivalent weight (EW) of less than 800g/mol, preferably less than 500 g/mol.

- 20 16. A conductive polymer and a support material for the polymer, wherein said polymer includes: polyaryletherketone and/or polyarylethersulphone units; and units of formula $-O-Ph_n-O-$ (XX) wherein Ph represents a phenyl group and n represents an integer of 2 or greater and wherein Ph groups of units (XX) are sulphonated.

- 25 17. A fuel cell or electrolyser incorporating a composite membrane according to any preceding claim.

- 30 18. A method of making a composite membrane according to any of claims 1 to 16, the method comprising causing a conductive polymer as described in any of claims 1 to 16

to be associated with a support material as described in any of claims 1 to 16.

19. A method according to claim 18, which includes
5 impregnating porous support material with conductive polymer.

20. A method according to claim 18 or claim 19, wherein a first solvent formulation comprises a polar aprotic
10 solvent in which a conductive polymer is provided and said support material is a material (e.g. a polyetheretherketone fabric or a polyetherketone microporous membrane) which is not soluble in said polar aprotic solvent, wherein the method includes a step of
15 contacting said support material with said first solvent formulation.

21. A method according to claim 18 or claim 19, wherein said support material is a fabric and the method includes
20 a step of contacting the fabric with a first solvent formulation comprising a first solvent and said conductive polymer, wherein said first solvent and said support material are selected so that the first solvent solubilizes a surface of the support material.

22. A method according to claim 21, wherein said first solvent is capable of functionalising said support material to provide ion-exchange sites on the surface thereof.

23. A method according to claim 22, wherein said first solvent includes less than 99% acid.

24. A method according to claim 18 or claim 19, the method including:

5 contacting said support material with a solvent formulation comprising a first solvent which solubilizes the support material; and
 contacting the support material with a second solvent to cause phase inversion and render said support material porous.

10 25. A method according to claim 24, wherein said conductive polymer is provided in a third solvent and caused to penetrate pores in the support material.

10070825689302

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 March 2001 (22.03.2001)

PCT

(10) International Publication Number
WO 01/19896 A1

(51) International Patent Classification⁷: C08G 65/48,
C08J 5/22, H01M 6/18, 10/40, 8/10, 2/16

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(21) International Application Number: PCT/GB00/03449

(72) Inventors; and

(22) International Filing Date:

8 September 2000 (08.09.2000)

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(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

PCT/GB/02833

10 September 1999 (10.09.1999) GB

0006884.1

22 March 2000 (22.03.2000) GB

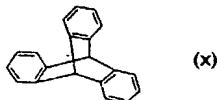
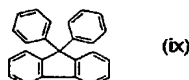
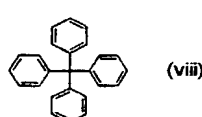
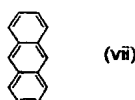
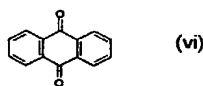
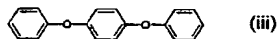
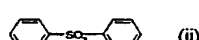
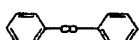
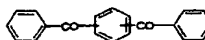
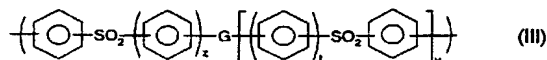
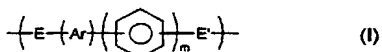
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(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,

[Continued on next page]

(54) Title: COMPOSITE ION-EXCHANGE MEMBRANES



(57) Abstract: A composite membrane for use as an ion-exchange membrane includes a conductive polymer and a support material for the polymer, said polymer having a moiety of formula (I) and/or a moiety of formula (II) and/or a moiety of formula (III), wherein at least some of the units I, II and/or III are functionalized to provide ion exchange sites; wherein the phenyl moieties in units I, II, and III are independently optionally substituted and optionally cross-linked; and wherein m, r, s, t, v, w and z independently represent zero or a positive integer, E and E' independently represent an oxygen or a sulphur atom or a direct link, G represents an oxygen or sulphur atom, a direct link or a -O-Ph-O- moiety where Ph represents a phenyl group and Ar is selected from one of the following moieties (i)*, (i) to (x) which is bonded via one or more of its phenyl moieties to adjacent moieties.

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HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- *With international search report.*
- *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

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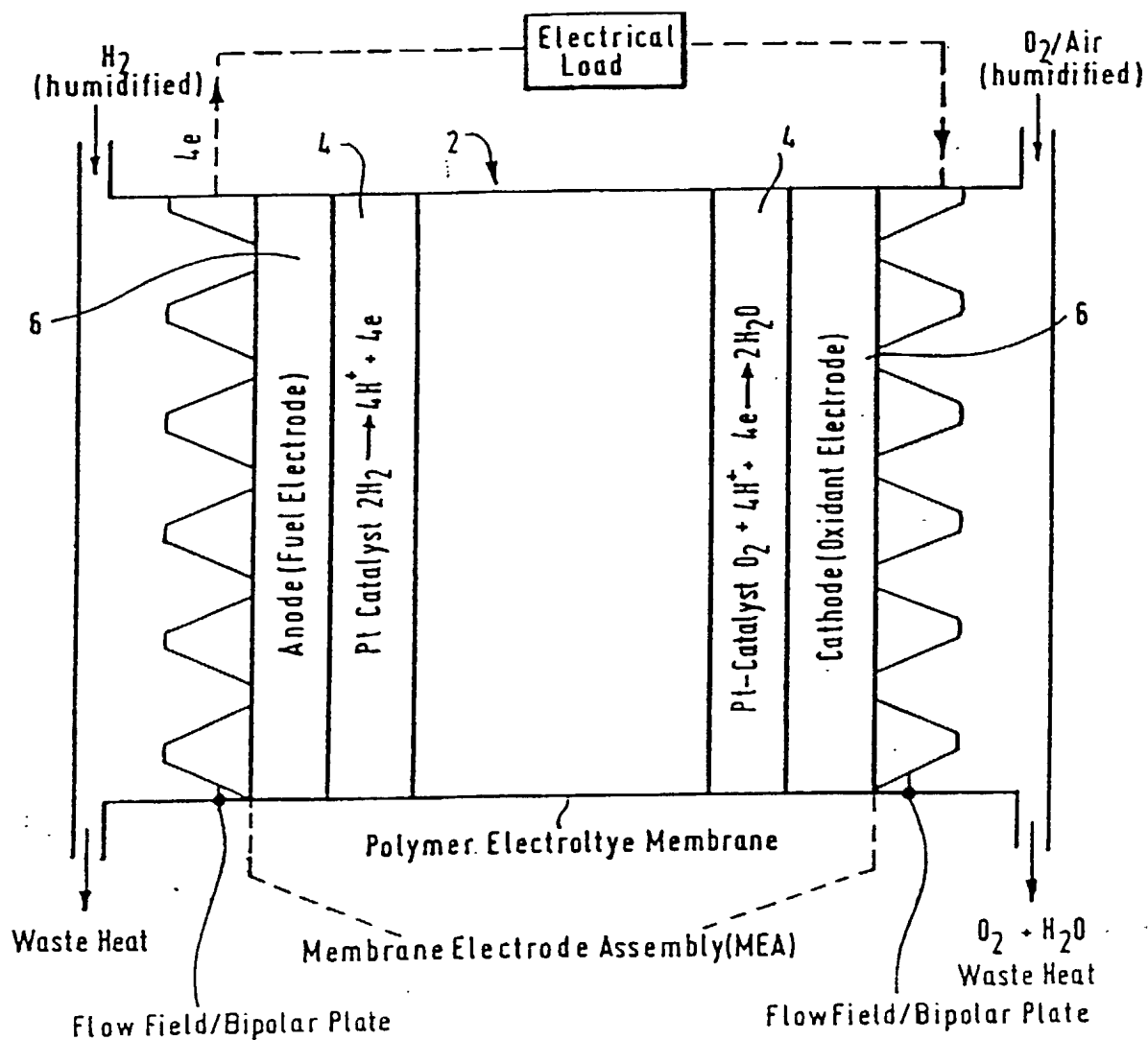


FIG.1.

687-104
APB/MER/W31Nixon & Vanderhye P.C. (10/99)
(Domestic Non-Assigned/Foreign) Page 1

RULE 63 (37 C.F.R. 1.63)
INVENTORS DECLARATION FOR PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

As a below named inventor, I hereby declare that my residence, mailing address and citizenship are as stated below next to my name, and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

COMPOSITE ION-EXCHANGE MEMBRANES

the specification of which (check applicable box(es)):

☐ is attached hereto
☐ was filed on _____ as U.S. Application Serial No. _____ (Atty Dkt. No. 687-104)
☒ was filed as PCT International application No. _____ PCT/GB00/03449 on 8 September 2000
 and (if applicable to U.S. or PCT application) was amended on _____

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose to the Patent Office all information known to me to be material to patentability as defined in 37 C.F.R. 1.56. I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed or, if no priority is claimed, before the filing date of this application:

Priority Foreign Application(s):

Application Number	Country	Day/Month/Year Filed
0006884.1	Great Britain	22 March 2000

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

Application Number	Date/Month/Year Filed
--------------------	-----------------------

I hereby claim the benefit under 35 U.S.C. 120/365 of all prior United States and PCT international applications listed above or below:

Prior U.S./PCT Application(s):

Application Serial No.	Day/Month/Year Filed	Status: patented pending, abandoned
PCT/GB00/03449	8 September 2000	
PCT/GB99/02833	10 September 1999	

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon. And on behalf of the owner(s) hereof, I hereby appoint **NIXON & VANDERHYE P.C., 1100 North Glebe Rd., 8th Floor, Arlington, VA 22201-4714, telephone number (703) 816-4000 (to whom all communications are to be directed)**, and the following attorneys thereof (of the same address) individually and collectively owner's/owners' attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent: Larry S. Nixon, 25640; Arthur R. Crawford, 25327; James T. Hosmer, 30184; Robert W. Faris, 31352; Richard G. Besha, 22770; Mark E. Nusbaum, 32348; Michael J. Keenan, 32106; Bryan H. Davidson, 30251; Stanley C. Spooner, 27393; Leonard C. Mitchard, 29009; Duane M. Byers, 33363; Jeffrey H. Nelson, 30481; John R. Lastova, 33149; H. Warren Burnam Jr., 29366; Mary J. Wilson, 32955; J. Scott Davidson, 33489; Alan M. Kagen, 36178; Robert A. Molan, 29834; B. J. Sadoff, 36663; James D. Berquist, 34776; Updeep S. Gill, 37334; Michael J. Shea, 34725; Donald L. Jackson, 41090; Michelle N. Lester, 32331; Frank P. Presta, 19828; Joseph S. Presta, 35329; Joseph A. Rhoa, 37515; Raymond Y. Mah, 41426; Chris Comuntzis, 31097; Gary T. Tanigawa, 43180. I also authorize Nixon & Vanderhye to delete any attorney names/numbers no longer with the firm and to act and rely solely on instructions directly communicated from the person, assignee, attorney, firm, or other organization sending instructions to Nixon & Vanderhye on behalf of the owner(s).

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☒ See attached sheet(s) for additional inventor(s) information!!

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